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JANUARY 23, 1989

CHEMICAL & ENGINEERING

NEWS

Detergents

Higher raw material costs spur new formulations
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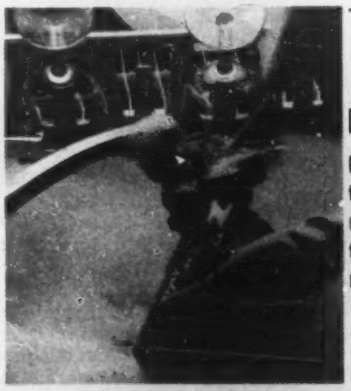

Product Report

More detergent makers are turning to new formulations in effort to maintain cost-performance levels of their products in face of rising raw material prices. **Page 29**

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LETTERS

Radiation epidemiology, extrapolation, and opinion

SIR: John W. Gofman asserts (C&EN, Sept. 26, page 74) that "the linear, no-threshold model of cancer induction by ionizing radiation may underestimate cancer risk, but not overstate it—contrary to" observations by R. J. Hickey (C&EN, May 23, page 2). Gofman adds that human epidemiological evidence "is the final reality check on hypotheses" and that "excess cancer occurs in human populations even from the slowest and lowest possible rates of delivery." Previously, Gofman stated [*Nuclear News*, **25**(13), 20 (1982)] that "scientifically it is thoroughly reasonable to say that cancer and leukemia induction by radiation is proportional to dose right down to the lowest conceivable doses." Such a position rejects the well-established biophysical phenomenon of radiation hormesis, which has been reported in depth by T. D. Luckey ["Physiological Benefits from Low Levels of Ionizing Radiation," *Health Phys.*, **43**, 771 (1982); "Hormesis from Ionizing Radiation," ibid., **46**, 705 (1984); "Hormesis bei Krebsinduktion durch radioaktive Strahlung hoher Ionizationsdichte," *Z. Phys. Med. Baln. Med. Klim.* (Sonderhelf 1), **13**, 11 (1984); "Beneficial Physiologic Effects of Ionizing Radiation," Leppin, W., et al., editors, "Die Hypothesen im Strahlenschutz," Georg Thieme Verlag, Stuttgart, page 184 (1985)].

Human radiation epidemiology reports imply health benefits from low-level radiation [for example, Hickey, R. J., Bowers, E. J., et al., "Low-Level Ionizing Radiation and Human Mortality: Multiregional Epidemiological Studies. A preliminary report," *Health Phys.*, **40**, 625 (1981); "Ionizing Radiation and Human Mortality: Multivariate Analysis of U.S. State Data," *Am. J. Phys. Anthropol.*, **54**, 233 (1981); "Radiation Hormesis, Public Health, and Public Policy: a Commentary," *Health Phys.*, **44**, 207 (1983)]. H. F. Henry noted ["Is All Nuclear Radiation Harmful?" *Health Phys.*, **43**, 767 (1982)] that he had commented earlier ["Is All Nuclear Radiation Harmful?" *J. Am. Med. Assoc.*, **176**, 671 (1961)] on health benefits of low-level radiation. Other aspects of the controversy were reported by R. J. Hickey, E. J. Bowers, and I. E. Allen ["TMI Psychological Impact," *Nuclear News*, **25**(7), 28 (1982); "Creative Statistics," ibid., **25**(10), 25 (1982); "Statistical Fantasy," ibid., **25**(14), 49 (1982)]. See also Hoffer, P. B., Gottschalk, A., Zaret, B. L., editors, "The Year Book of Nuclear Medicine—1984," Year Book Medical Publishers, Chicago, page 199 (1984). The controversy was also discussed in "Risks Associated with Exposure to Radiation: Science, Pseudoscience, and Opinion," *Health Phys.*, **49**, 949 (1985); in "Radiation Protective Effect of Bacterial Endotoxins: Nonspecific Immunity," *Health Phys.*, **49**, 1013 (1985); in "Health Benefits from Low-Level Ionizing Radiation: Radiation Hormesis and the Question of Stimulation of Immunological Efficiency," *Z. Phys. Med. Baln. Med. Klim.* (Sonderheft 1), **17**, 8 (1988); and in "Cigarettes, Rn, Cancer,—and Health Physics," *Health Phys.*, **55**, 821 (Nov. 1988). Extensive observed evidence contradicts Gofman's allegations.

Reports presented at the International Symposium on Biological and Therapeutical Effects of Radon, held in Bad Hofgastein, Austria, October 1987, have been published. Examples are Deetjen, P., "Biologische und Therapeutische Effekte von Radon," *Z. Phys. Med. Baln. Med. Klim.* (Sonderheft 1), **17**, 5 (1988); Andrejev, S. V., "Über einen Möglichen Wirkungs Mechanismus der Thermalstollen-Behandlung in Böckstein (Österreich)," ibid., **17**, 54 (1988); Bogoljubov, V. M., "The Clinical Aspects of Radon Therapy," ibid., **17**, 59 (1988); Morinaga, H., "Medical Experiences in the Japanese Radon Spa, Misasa," ibid., **17**, 67 (1988).

Insofar as I am aware, the 1987 Bad Hofgastein symposium and the findings have not been reported in any newspaper or technical news journal in the U.S. Why? Among European press reports were Mayrhofer, F., "Die Wohltätigkeit des Edelgases Radon," *Salzburger Nachrichten*, Oct. 10, 1987, and "Zur modernen Radontherapie," *Wiener Zeitung* (Vienna), Nov. 27, 1987.

P. Deetjen, of the Research Institute Gastein-Tauernregion, Badgastein, Austria, has issued an English language pamphlet on "Scientific Principles of the Health Treatments in Badgastein," 3rd edition, 1984, 14 pages. This and other publications regarding radon health and vacation resorts and spas in Austria may be obtained from Kurdirektor Joseph J. Flatscher, Kurverwaltung Badgastein, Haus Austria, A-5640 Badgastein, Austria.

In view of the controversy regarding health effects of low-level ionizing radiation, including propaganda, it is enlightening to examine the published Garland Lecture of E. W. Webster, "On the Question of Cancer Induction by Small X-Ray Doses," *Am. J. Roentgenology*, **137**, 647 (1981). He states, "There is no proven body of fact that establishes an increase in human cancer after low doses of X or gamma radiation such as those received environmentally, occupationally, or from medical diagnostic procedures; that is, radiation levels below about 10 rad (0.1 Gy)."

Tough problems hinder Soviet chemical growth

The U.S.S.R. is among the world's top producers of chemicals and chemical products. In 1986, for example, it led the world in output of chemical fertilizers, synthetic rubber, and ammonia, and was one of the leaders in plastics, sulfuric acid, and sodium hydroxide production. Chemical output has grown much faster than that of Soviet industry overall.

And yet, says a new study, as with the rest of Soviet industry, a variety of tenacious problems is hindering growth of the chemical sector and preventing it from reaching its potential. These problems include technological backwardness, difficulties in assimilating new technology, delays and cost overruns in plant construction, overly rigid central planning, poor product quality, irrational pricing, supply shortages of raw and intermediate materials, excessive managerial conservatism, and insufficient skilled labor.

In response, the Soviets have launched a comprehensive program for "chemicalization" of their economy by the year 2000. The program calls for growth of 30 to 32% in chemical output during the current five-year plan (1986–90), with investment slated to rise 50%. Among the fastest growing sectors are to be plastics (up 36%), man-made fibers (33%), pesticides (30%), and mineral fertilizers (26%), with pharmaceuticals and paints and lacquers also targeted for rapid growth.

However, the study notes, relatively weak overall economic growth in three of the past four years and a hard-currency crunch (due, in part, to lower hard-currency revenues from oil exports) have delayed construction of many new Soviet chemical facilities, especially those bought from the West. The Soviets have shifted emphasis recently to joint ventures with Western firms, rather than the massive turnkey plant contracts they signed with Western firms in the 1970s and 1980s.

Chemical exports to nonsocialist countries also are disappointing, as the Soviets suffer from a squeeze on both cost and revenue sides. Meanwhile, chemical imports from nonsocialist countries are rising rapidly. And, contrary to the five-year plan goals, investment in the chemical and petrochemical branches is stagnating.

Pharmaceuticals lead growth of Soviet chemical industry

Growth in gross output	1987	1986	1985	1984	1983	1982	1981
ALL INDUSTRY	4.0%	4.7%	3.9%	4.0%	4.2%	3.3%	3.4%
CHEMICAL AND PETROCHEMICAL INDUSTRY, TOTAL	4.4	5.8	5.3	5.2	5.9	3.0	5.5
CHEMICALS	5.0	7.1	5.3	5.6	6.8	3.8	6.7
Mining chemicals	4.6	7.5	5.7	4.3	5.0	0	4.8
Basic chemicals	4.9	6.8	6.1	4.6	8.1	4.0	7.3
Man-made fibers	2.9	7.7	1.7	5.0	8.5	4.0	5.5
Plastics, synthetic resins	5.1	9.6	5.9	10.3	5.9	−1.9	3.5
Paints, varnishes	4.8	3.8	4.0	6.0	4.4	1.3	4.7
Synthetic dyes	3.8	6.3	5.9	4.2	4.4	2.5	5.2
Pharmaceuticals	6.6	7.9	7.6	7.6	6.1	6.9	7.4
PETROCHEMICALS	2.5	3.4	4.0	4.1	2.8	2.4	3.0
Basic organic synthesis products	2.1	8.1	8.4	7.9	8.1	3.5	2.7
Tires	3.4	2.7	2.8	2.8	1.9	3.5	3.1
Rubber, asbestos	1.6	3.8	5.0	3.1	3.2	3.8	1.1
MINERAL FERTILIZERS (100% active substance)	4.6	4.3	8.0	3.5	11.2	3.0	4.7

Source: PlanEcon Inc. based on official Soviet figures

The comprehensive 222-page study on Soviet chemical production, trade, and investment was prepared by PlanEcon Inc., a Washington, D.C.-based firm specializing in research on the Soviet and East European economies. Selling for $2500, the study will appear each fall.

PlanEcon is also involved in an effort to inform U.S. chemical firms about the opportunities opened by glasnost and perestroika—the new Soviet policies of openness and restructuring. The Chemical Manufacturers Association and PlanEcon will cosponsor a conference in Washington, D.C., in March on Soviet chemical and petrochemical production and trade, on prospects for chemical equipment and process imports, and on joint ventures. PlanEcon research director Jan Vanous says U.S. firms are likely to find greater opportunities in chemicals and petrochemicals than in other sectors.

Soviet chemical exports to nonsocialist countries are one of the major disappointments pictured in the study. In 1987, such exports totaled just $1.25 million, up only 8.6% from 1980. The Soviets continue to export mainly basic, low-value-added products rather than moving, as planned, into specialty, high-value-added products, such as dyes, paints, explosives, photographic products, pesticides, and rubber products.

Unlike Western petrochemical producers, who are enjoying a boom based on low world feedstock prices, the Soviets are taking a beating on exports of bulk petrochemicals and products based on oil and gas, such as ammonia and urea. This is because, insulated from world prices, the Soviets have faced steadily rising domestic oil and gas costs, but have had to cope with falling prices on the world market for the final products. As a result, Soviet exports of ammonia and urea based on natural gas have plummeted from 51% of nonsocialist exports in 1981 to about 23% in 1987.

As for imports, the study says imports of chemicals and fertilizers from nonsocialist countries will soar 12% a year in 1988–92. This will furnish opportunities to supply high-priority Soviet needs for plastics, pesticides, and other materials.

Richard Seltzer

Industrial detergents (left) frequently contain materials found in household cleaners; a major building block in dishwasher detergents (below) is linear alkylbenzene

Higher Costs Spur New Detergent Formulations

Bruce F. Greek, C&EN Houston, and
Patricia L. Layman, C&EN London

Reformulation is getting more emphasis in the detergent industry than it has in several years. Increased raw material costs and detergent makers' reluctance to pass on those costs to consumers have led to subtle, yet significant, changes in how much of what goes into powder, liquid, and bar soaps and detergents.

By changing formulations in these significant and subtle ways, detergent makers and marketers are trying to improve cost/performance characteristics of their cleaning products. Generally, formulations have became more complex as a result of these efforts to enhance performance, specifically to impart greater multifunctionality to detergent products while keeping costs down.

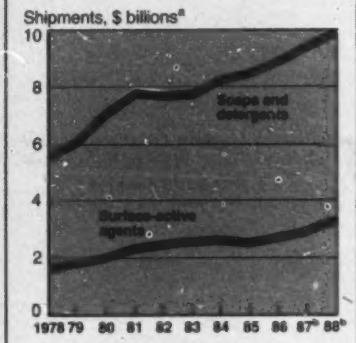
Detergent producers choose from a growing number of surfactants, builders, and other materials to provide the performance and aesthetic properties now expected from detergents. Costs of many of their raw materials have risen, with more increases forecast for later this year. However, material suppliers are offering improved products to maintain the cost/performance levels of detergent products in the extremely competitive retail markets for household cleaning and personal care products.

The detergent industry undergoes changes through evolution, as improved materials become available that meet the demands from consumers for such diverse performance characteristics as high cleaning efficiency and maximum convenience—all obtained at lowest possible cost. However, no revolutionary developments hit the detergent industry last year and none are expected this year.

One example of the trend in evolution in products offered by the detergent industry is the growth in sales of heavy-duty liquid detergents for household laundry. From about 15% of the total market in 1978, heavy-duty liquids have grown to more than 40% of the market this year.

Development of surfactants and other materials capable of giving a performance equal to that of the powdered products has been critical in this growth. Another critical factor has been development of formulating technology to make the components perform as desired (tak-

Value of soaps, surfactants about doubled in decade



a Products classified as soaps, cleaners, and toilet goods (SIC 284) produced by all industries. b Estimated.
Source: Department of Commerce

ing into account the frequent synergism between components). Consumer acceptance has grown significantly because of the convenience provided by single-dose application of liquid products. Many packages made for liquid detergents have a cap suitable for measuring the amount to add. The cap, designed to prevent residual detergent from running down the outside of the container, is known as the internally draining cap, one example of a packaging engineering development.

As the number of women working outside the home grew during the past decade, convenience took on much greater importance. Laundry methods involving a presoak, a washing, and a rinse, during which a fabric softener is added, no longer are acceptable. A surfactant, builder, bleach, softener, antistatic agents, and other performance chemicals now must be in the product added at the beginning of a wash, with no further attention given to the process until the clothes are moved to a dryer.

Demand for the multifunctional products has become firmly established in U.S. markets for many cleaning products other than household laundry detergents, and the trend is emerging in the other major regions of the world having large demand for detergents, especially Japan and Western Europe.

To keep bringing better products to market, the product formulators continually make decisions on which components they use, while taking into account the exacting relationship between cost and performance. Formulators try to develop particular niches for their products, while keeping the products as broadly applicable as possible. This allows maximum production volume for economies of scale.

Formulators now are receiving more help from their suppliers, who represent most of the major producers of chemicals. These suppliers are bringing more of the technical expertise used in making chemicals for many other industries into providing improved products for the detergent, cleaners, cosmetics, and related industries.

The application of chemical technology to cleaning preparations during the past generation has brought a huge boost to the materials available for use in the product. The American Chemical Society's manual of commercially available chemicals, *Chemcyclopedia*, includes more than 375 compounds and mixtures in the section on surfactants alone. Proprietary surfactants likely increase substantially the number used in commerce.

As the number of materials available for making cleaning products has mushroomed, so have the volume and the value of the materials. The value of shipments of soaps and detergents exceeded $10 billion for the first time in 1988, estimates Leo R. McIntyre of the Department of Commerce. That amount is 81% higher than the value of shipments in 1978. Even in terms of 1988 dollars, the value of last year's shipments was 7.3% ahead of that of 1987 (an estimated $9.4 billion).

The value of shipments of surfactants more than doubled between 1978 and 1988, McIntyre says, rising from $1.55 billion to almost $3.4 billion in 1988. The increase in value of shipments for surfactants during the past two years has been nearly twice as great as for all soaps and detergents, rising 25% between 1986 and 1988.

Close to 7 billion lb of formulated laundry detergents was used in the U.S. last year, mostly in households, McIntyre estimates. To reach this level, consumption has grown an average of more than 4% a year since 1980. In addition, use of automatic dishwasher detergents reached about 635 million lb last year.

The outlook for 1989 is for a 3.9% increase in the value of shipments of soaps and detergents, according

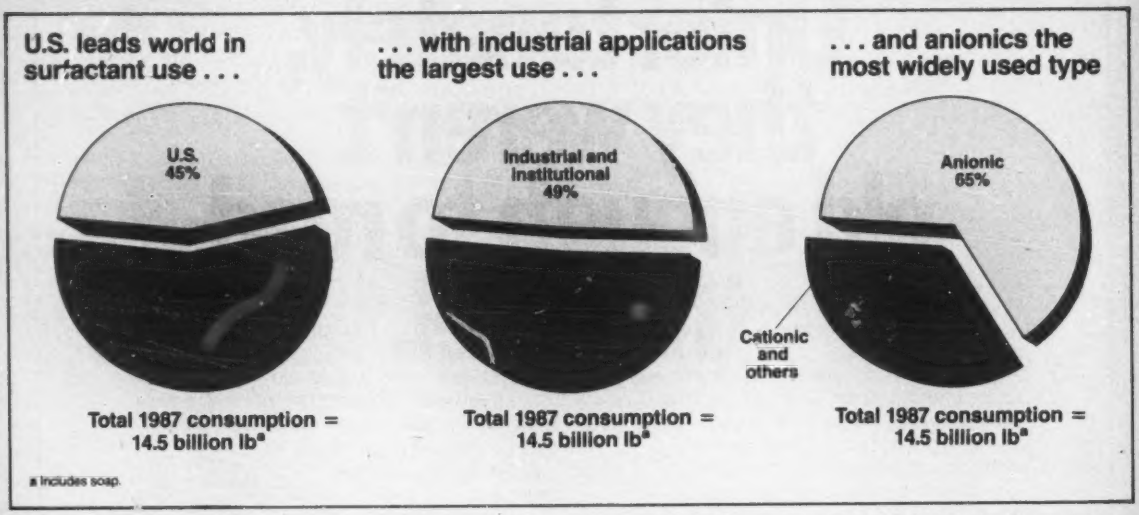
Surfactants fit generally into four classes

Anionics. Still at about 60% of U.S. surfactant production, anionics have slowly lost share of the increased market. The active detergency is in the large anion part of the molecule. However, the anion must be neutralized with an alkali before full detergency is obtained. Anionics also are the most widely used surfactants in formulated detergents. The largest volume anionics are based on alkylates of benzene and propylene trimer or tetramer.

Cationics. As implied by the name, the detergency in this class of compounds is in the cation. Because their efficiency in cleansing falls below many anionic and nonionic surfactants, they find less use in formulated detergents. The major uses are in specialized products that benefit from the presence of a surfactant. Most cationics are derivatives of amines.

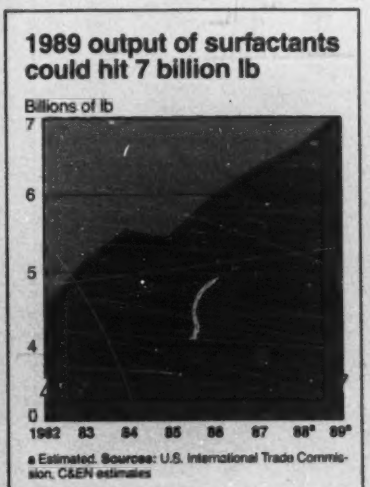
Nonionics. The majority of nonionic surfactants are made by condensing a hydrophobe and ethylene oxide and then adding more ethylene oxide molecules to give a water-soluble product. The number of ethylene oxide molecules in the product surfactant can average 10 to 15. Several kinds of hydrophobes are used, such as fatty alcohols and acids, amines, and amides.

Amphoterics. This low-production class of surfactants has molecules that contain both an anionic and a cationic group. Depending on components of the molecule, amphoterics having various characteristics can be tailored into the final cleaning product or can provide fabric-softening properties. Examples of amphoterics are derivatives of imidazolines and betaines. Amphoterics' high cost limits their use.


U.S. leads world in surfactant use . . .
U.S. 45%
Total 1987 consumption = 14.5 billion lb[a]
. . . with industrial applications the largest use . . .
Industrial and institutional 49%
Total 1987 consumption = 14.5 billion lb[a]
. . . and anionics the most widely used type
Anionic 65%
Cationic and others
Total 1987 consumption = 14.5 billion lb[a]
a Includes soap.

to McIntyre. Longer-term prospects call for real growth (after inflation) to average 3% per year between 1989 and 1995. Sales of heavy-duty liquid laundry detergents are forecast to exceed sales of powdered laundry detergents by 1993.

Household cleaning products alone likely topped $9 billion in sales last year. In 1987, sales totaled $8.9 billion, up about 2.7% from 1986, according to a recent study by consultants Kline & Co. of Fairfield, N.J. Much of the growth in sales of household cleaning products comes from laundry detergents, particularly those in liquid form. Another fast-growing household cleaning product is liquid automatic dishwashing detergents, which reached about a quarter of the dollar sales volume for all automatic dishwashing detergents in 1987, according to the Kline study.



Further changes in demand for household cleaners are expected from diverse influences, such as shifts in population demographics, increased consumer demand for convenience in use of products, producer consolidation through acquisitions and divestitures, more proliferation of brands, and emergence of new segments in cleaners. Shifts in demographics include factors other than increases in number of women working, the Kline study shows—for instance, a growing proportion of single-person and older-person households. New segments in cleaners that are emerging include products that add convenience, such as the unitized dose packages of laundry detergents, cleaning wipes for bathroom cleaning, and cleaners specifically for microwave ovens.

Besides household cleaners, two other major categories of cleaners are addressed by detergent producers—personal care products and industrial and institutional cleaning products. Personal care products may contain materials found in household cleaners, although their formulations generally are less complex. Industrial and institutional products also may be similar to household products, and may even be the same product.

Although the same materials generally may be used in cleaners, there is a wide variation in formulation, depending on the kind of cleaning and circumstances of the cleaning. Variations are especially notable in different regions of the world. Some products, such as personal care items, may be a surfactant and one or two other components. Others, such as laundry detergents, may contain 10 to 15 ingredients, some in concentrations ranging up to 50% of the total, and others in only a few parts per million. Excluding fillers and water, some of the components in cleaners are of major interest to the formulators as key performers, whereas others have minor roles.

Household cleaners, particularly laundry detergents, receive most of the attention in development activities because of the competitive nature of markets and because the large volume permits relatively better margins. Components of these cleaners fall into three major categories: surfactants, to remove dirt and other unwanted materials from clothes; builders, to treat the washwater to improve the efficiency of surfactants; and additives, which may include bleaches, bleach activators, antiredeposition agents, optical brighteners, antistatic agents, and fabric softeners.

Because of their importance, surfactants receive more development effort than any other components of cleaners. Soap, known for 4500 years but used mainly as a cosmetic for the first 3500 years, remains the

Household detergent formulations vary in U.S., Western Europe, and Japan

Component	Examples	Composition, % U.S. With builders	U.S. Without builders	Western Europe With builders	Western Europe Without builders	Japan With builders	Japan Without builders
HEAVY-DUTY POWDERED DETERGENTS							
Anionic surfactants	Alkylbenzene sulfonates	0–15%	0–20%	5–10%	5–10%	5–15%	5–15%
	Fatty alcohol sulfates	—	—	1–3	—	0–10	0–10
	Fatty alcohol ether sulfates	0–12	0–10	—	—	—	—
	Alpha-olefin sulfonates	—	—	—	—	0–15	0–15
Nonionic surfactants	Alkyl and nonylphenyl poly(ethylene glycol) ethers	0–17	0–17	3–11	3–6	0–2	0–2
Suds-controlling agents	Soaps, silicon oils, paraffins	0–1.0	0–0.6	0.1–3.5	0.1–3.5	1–3	1–3
Foam boosters	Fatty acid monoethanol amides	—	—	0–2	—	—	—
Chelators (builders)	Sodium tripolyphosphate	23–55	—	20–40	—	10–20	—
Ion exchangers	Zeolite 4A, poly(acrylic acids)	—	0–45	2–20	20–30	0–2	10–20
Alkalies	Sodium carbonate	3–22	10–35	0–15	5–10	5–20	5–20
Cobuilders	Sodium citrate, sodium nitriliotriacetate	—	—	0–4	0–4	—	—
Bleaching agents	Sodium perborate	0–5	0–5	10–25	20–25	0–5	0–5
Bleach activators	Tetraacetylethylenediamine	—	—	0–5	0–2	—	—
Bleach stabilizers	Ethylenediaminetetraacetate	—	—	0.2–0.5	0.2–0.5	—	—
Fabric softeners	Quaternary ammonium compounds	0–5	0–5	—	—	—	0–5
Antiredeposition agents	Cellulose ethers	0–0.5	0–0.5	0.5–1.5	0.5–1.5	0–2	0–2
Enzymes	Proteases, amylases	0–2.5	0–2.5	0.3–0.8	0.3–0.8	0–0.5	0–0.5
Optical brighteners	Stilbene derivatives	0.05–0.25	0.05–0.25	0.1–0.3	0.1–0.3	0.1–0.8	0.1–0.8
Anticorrosion agents	Sodium silicate	1–10	0–25	2–6	2–6	5–15	5–15
Fragrances		a	a	a	a	a	a
Dyes and blueing agents		a	a	a	a	a	a
Formulation aids		0–1.0	0–1.0	—	—	—	—
Fillers and water	Sodium sulfate	Balance	Balance	Balance	Balance	Balance	Balance
HEAVY-DUTY LIQUID DETERGENTS							
Anionic surfactants	Alkylbenzene sulfonates	5–17	0–10	5–7	10–15	5–15	—
	Fatty alcohol ether sulfates	0–15	0–12	—	—	5–10	15–25
	Soaps	0–14	—	—	10–15	10–20	—
Nonionic surfactants	Alkyl poly(ethylene glycol) ethers	5–11	15–35	2–5	10–15	4–10	10–35
Suds-controlling agents	Soaps	—	—	1–2	3–5	—	—
Foam boosters	Fatty acid alkanolamides	—	—	0–2	—	—	—
Enzymes	Proteases	0–1.6	0–2.3	0.3–0.5	0.6–0.8	0.1–0.5	0.2–0.8
Builders	Potassium diphosphate, sodium tripolyphosphate	—	—	20–25	—	—	—
	Sodium citrate, sodium silicate	6–12	—	—	0–3	3–7	—
Formulation aids	Xylene sulfonates, ethanol, propylene glycol	7–14	5–12	3–6	6–12	10–15	5–15
Optical brighteners	Stilbene derivatives	0.1–0.25	0.1–0.25	0.15–0.25	0.15–0.25	0.1–0.3	0.1–0.3
Stabilizers	Triethanolamine	—	—	—	1–3	1–3	1–5
Fabric softeners	Quaternary ammonium salts	0–2	0	—	—	—	—
Fragrances		a	a	a	a	a	a
Dyes		a	a	a	a	a	a
Water		Balance	Balance	Balance	Balance	Balance	Balance

a Component may be present in very small concentrations. Source: Henkel

most used surfactant today, despite the enormous development of synthetic surfactants during the past 40 years. However, soap has relatively few development efforts under way except in the improvement of purity and processing.

As a group, however, the synthetic materials far exceed soap in production volume. The development of synthetic surfactants came about because of soap's high sensitivity to water hardness and its tendency to leave unwanted waste products and an odor in clothes.

The synthetic surfactants and their formulated products—synthetic detergents—became available commercially in Germany in the late 1920s but didn't begin to sell in large volumes in developed countries until after World War II. The alkylation processes used to make high-octane components of aviation gasoline during World War II led to development of the branched chain alkylbenzene sulfonates. Then, synthetic detergents of many kinds were on their way. The first synthetics—fatty alcohol sulfates and

derivatives made by reacting these alcohols with ethylene oxide—and the linear alkylbenzene sulfonates continue to be important in today's surfactant markets. Linear alkyl chains replaced branched chains to improve greatly biodegradability.

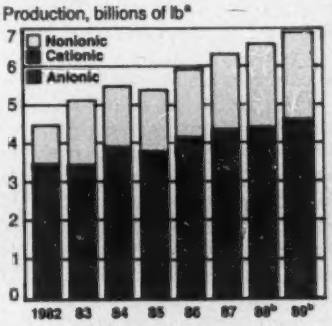
U.S. production of synthetic surfactants in 1989 likely will exceed 7 billion lb for the first time, up 6% from the estimated 6.6 billion lb produced last year. That growth would about match growth during both 1986 and 1987. Total production in 1987 was 6.27 billion lb, according to the U.S. International Trade Commission (ITC). More than 58% of U.S. production of surfactants in 1987 was anionics, ITC says. About 655 million lb, or 10% of production, was cationic surfactants, and the remainder was nonionics, except for a small quantity (33 million lb) of amphoteric surfactants. About 62% of production of surfactants was sold in 1987, having a value of more than $1.7 billion (the remainder was consumed captively).

Production of anionic types of surfactants grew very little in 1987, increasing only 13 million lb from 1986 to a total of 3.67 billion lb. Cationic surfactant output rose 33% from 1986 to 655 million lb in 1987 but has the smallest base of the three largest categories. Nonionic surfactant production rose 11% to 1.91 billion lb in 1987.

As in the past, the various lignin sulfonates held their position as the largest-volume anionic surfactants, but not by much, at more than 880 million lb. The various sulfuric acid esters and salts, which include numerous sulfated alcohols and ethers as the result of ethoxylation, had a total production of about 800 million lb. Alkylbenzene sulfonates (mostly dodecyl derivatives) ranked third, at more than 735 million lb.

Nearly all cationic surfactants are amine or amide derivatives or are quaternary ammonium salts, with few individual compounds having significant production volume. The nonionics, at more than 800 million lb, are dominated by various ethoxylated linear alcohols, many of which are mixtures of alcohols before being ethoxylated. Benzenoid ethers, especially ethoxylated nonylphenol, accounted for more than 500 million lb of nonionics production in 1987. Various carboxylic acid esters, at more than 300 million lb, made up much of the remainder of nonionics production.

Nonionic and cationic surfactants show gains



a Excludes small quantity of amphoteric surfactants. b Estimated. Sources: U.S. International Trade Commission, C&EN estimates

After soap, the most used surfactants in North America, Western Europe, and Japan are linear alkylbenzene sulfonates (LASs). According to estimates of West German detergent maker Henkel, 1987 consumption of LASs in those areas exceeded 2.15 billion lb. By far, the largest share of LASs consumed in the world is dodecylbenzene sulfonate, because that compound provides the best performance. Various other aromatic nuclei such as naphthalene, toluene, xylenes, and phenol are used in specialized products, and many other alkyl groups also may be used to make various surfactants.

LAS compounds compete with several other large-volume surfactants as one of the active components of cleaners. Their growth has varied during the 1980s as their cost and the cost of competing surfactants increased and decreased relative to each other. Currently, LAS demand appears to be growing more rapidly than in the recent past, because their cost has not increased so fast as the cost of competing alcohol sulfates, alcohol ether sulfates, alcohol ethoxylates, and other surfactants based on ethylene as the basic raw material. Benzene and propylene, basic raw materials for most linear alkylbenzenes, increased less in price last year than did ethylene,

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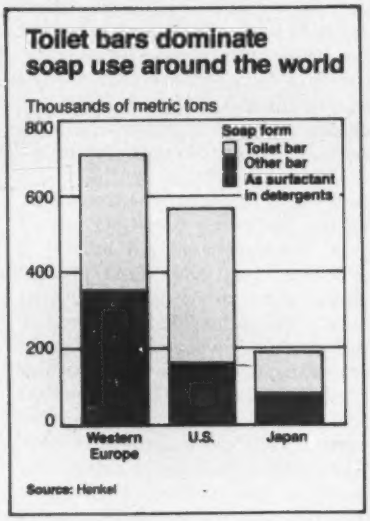
the price of which has more than doubled in just over a year. A part of the extensive reformulation of detergent products that began in 1988 and is expected to continue this year is the direct result of cost hikes of ethylene-based surfactants.

Often LASs are combined with other surfactants in a detergent formulation to give desired cost/performance. Included in the cost considerations are processing cost advantages, such as the ease of spray drying if a powdered product is being made. One of LASs' performance disadvantages that can offset their cost advantage is their greater sensitivity to water hardness than that of alcohol ether sulfates or some of the nonionic surfactants. Because sodium tripolyphosphate or other builders are seldom used in heavy-duty liquid detergent formulations to soften water, makers of these detergents have tended to use more alcohol ethoxylates than LASs. The more rapid shift toward liquid laundry detergents during the mid-1980s and an earlier increase in cost of LASs slowed growth in demand at that time. More recently, further declines in the use of phosphate builders have caused detergent formulators to increase surfactant concentrations. At the same time, the synergistic effect of LASs and alcohol ethyoxylates in cleaning performance became more widely recognized, increasing demand for LASs.

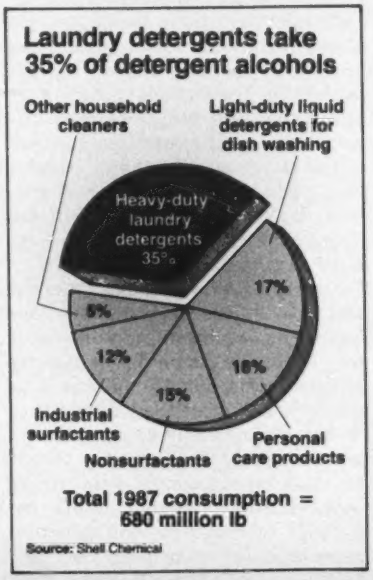
LASs consumption ranges across the many cleaning formulations because of their high cost/performance effectiveness. This property is behind the substantial growth of linear alkylbenzenes (LABs) forecast by Colin A. Houston & Associates, a consulting firm in Mamaroneck, N.Y. According to a recent study by the firm, worldwide demand for detergent alkylates, mostly LABs, will grow to 2.6 million metric tons by the year 2000, from 1.8 million metric tons in 1986. Most all of these alkylates become surfactants as a result of being sulfonated, and about 85% becomes a component of household cleaning products, primarily laundry detergents. Large developing countries such as India and China are fueling the growing global demand for LABs, according to Houston, whereas areas such as



North America and Western Europe have mature markets with moderate growth expected.

LABs will continue to replace branched-chain alkylbenzenes (BABs) in surfactants throughout the world because of the poor biodegradability of BABs. Although North America and Western Europe changed from BABs to LABs about 25 years ago, other regions of the world began the switch very recently. Only in Latin America will BABs consumption increase during the next decade, according to the Houston study.

To meet demands, a rapid increase



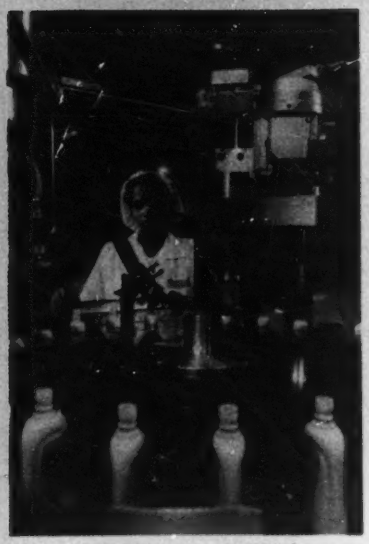
in capacity for LABs is under way in East bloc and Third World countries, Houston finds. Although LABs consumption in these countries will increase 800,000 metric tons by 2000, most of the intermediate will be supplied locally, tending to limit export opportunities for producers in industrially developed areas.

In the U.S., both major producers of LABs—Monsanto and Vista Chemical—have expansions under way to add more than 150 million lb to annual capacity. These expansions are the result of above average growth in demand for LABs since 1985, in the 5 to 6% range, says Anthony J. Zoglio, Monsanto's business manager for detergents and surfactants. The demand growth has come from both the limits on phosphate builders in the U.S. and from the shift toward heavy-duty liquids for laundry use, both developments causing formulators to increase the concentration of surfactant in detergents. However, longer term, Zoglio expects demand to grow more slowly, at 3 to 4% per year, as supplies of ethylene improve when plants under construction begin operation, price increases of ethylene-based surfactants slow down, and reformulation toward more use of LASs in detergents also slows down.

Vista believes that LABs' growth will continue at more than 5% in 1989. The company increased its LAB capacity 45 million lb last year and will add another 60 million lb to capacity this year, bringing its total to 490 million lb. A part of Vista's Baltimore, Md., detergent alkylate capacity will be used for specialty alkylates used as lubricant additives.

Vista also makes detergent alcohols, the derivatives of which are competitors of LASs in detergent formulations for various end uses. Besides Vista, producers include Shell Chemical (the largest), Ethyl, Procter & Gamble, and others with small capacities. These alcohols generally fall in the range of C_{12} to C_{18}, either synthetic or natural. The synthetics are based on ethylene or on *n*-paraffins separated from petroleum. The natural alcohols are based on coconut and palm oils and on tallow.

The synthetic alcohols are produced by several processes. One



Detergents filling line at British Petroleum's Unza plant in Malaysia

group of processes is based on the reaction of carbon monoxide and hydrogen with linear olefins, either alpha or internal, in the presence of a catalyst. Linear olefins are made either from ethylene or are recovered from suitable petroleum fractions, such as a kerosine cut, using molecular sieves.

Another group of commercial processes to produce detergent alcohol involves reaction of triethylaluminum and ethylene (the Ziegler technology) to build longer-chain triethyl aluminums, oxidation to alkoxides, and subsequent hydration to alcohols and aluminum hydroxide. These processes produce very high fractions of even-numbered carbon chain length linear alcohols. The coproduct aluminum hydroxide is usually recovered and sold as the oxide or another salt.

Detergent alcohols are made from natural sources by using methanol to break the triglycerides in vegetable oils and tallow to give methyl esters of the fatty acids and the coproduct glycerin. The esters then are hydrogenated, using a copper-based catalyst, to the alcohols and methanol, which is recycled. The mixture of alcohols, which may include chain lengths ranging from C_6 to C_{20} and higher, is fractionated to remove impurities and to give cuts of alcohols with the desired chain lengths.

Supply of raw materials for making synthetic detergent alcohols will easily meet demands, as capacity expansions continue. For example, Shell Chemical has added 50 million lb-per-year capacity to its unit at Geismar, La., bringing capacity there to 700 million lb per year. At the same time, Shell raised its detergent alcohol capacity 50 million lb per year to 600 million lb per year. A second linear alpha-olefin unit is under construction for Shell at Geismar. This unit will have a capacity of 535 million lb per year plus substantial, but undisclosed, internal olefins capacity when it starts up this spring.

The alcohols, often ethoxylated or reacted with other compounds first, are converted to derivatives useful as surfactants largely by reaction with sulfur trioxide, chlorosulfonic acid, or oleum. The products then are neutralized with base, mainly sodium salts.

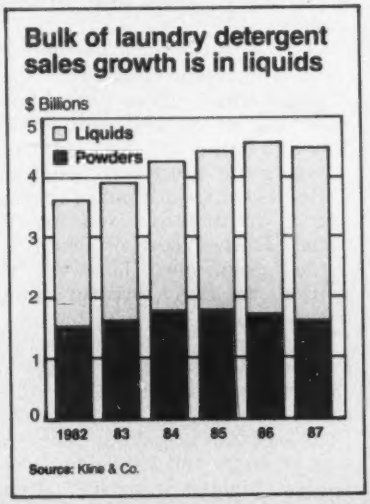
Between 80 and 90% of detergent alcohols are converted to surfactants. Four products—alcohol ethoxylates, alcohol sulfates, alcohol ether sulfates, and alkylglyceryl ether sulfonates—account for most of the surfactant uses, which include heavy-duty laundry detergents, light-duty liquid detergents (mostly for hand dishwashing), other household cleaners, various personal care products, and many institutional and industrial cleaners. Other derivatives of detergent alcohols may be used in detergent formulations, such as fabric softeners.

U.S. demand for surfactants based on detergent alcohols has grown about 3% annually between 1976 and 1986, says Jerry G. Moffett Jr., Shell Chemical's business manager for detergent products. While agreeing that the increased cost of ethylene-based surfactants has caused detergent manufacturers to reformulate to hold down cost increases, Moffett says that the total impact, as well as the longer-term impact, on these surfactants is as yet unclear.

Six surfactants account for most of market

Billions of lb	
Soap	3.25
Linear alkylbenzene sulfonates	2.15
Alcohol ethoxylates	1.05
Alkylphenol ethoxylates	0.85
Alcohol ether sulfates	0.75
Alcohol sulfates	0.55
TOTAL	8.60

Source: Henkel



Suppliers of materials for these surfactants have to counteract higher costs by offering better products. Shell Chemical, for example, has greatly increased the number of ethoxylates it makes, according to Moffett. Shell also has begun to offer grades of single-cut detergent alcohols such as C_{11}, C_{13}, and C_{15}.

In Western Europe, the shift to heavy-duty liquid laundry detergents has begun, but the share of the market is half or less than the share in the U.S. Some differences exist in detergent formulation in that region from the formulations used in the U.S. And Japan differs from both regions. Even so, many of the same kinds of surfactants are used in all three regions and are influenced by consumer demands that may differ from region to region.

The shift to heavy-duty liquid detergents, however, has caused a dramatic increase in surfactant concentration, according to René Carlotti, Shell's London-based business manager for detergents, higher olefins, and plasticizers. At this time, Carlotti says, ethoxylation capacity to make surfactants based on detergent alcohols is fully utilized in Western Europe, possibly limiting growth in the near term. However, Shell is adding capacity in the U.K. and

Spain; the unit in Spain is scheduled to go on stream in mid-1989. Other companies also are adding ethoxylation capacity in Western Europe.

The rise of heavy-duty liquid laundry detergents in Italy has been especially rapid, says Luciano Topi, commercial director of EniChem Augusta in Milan. This shift to liquid detergents in Western Europe is straining ethylene oxide supply, he adds. Ethylene supplies also are tight, and, although ethylene oxide for detergent products is a small part of the total ethylene market, the derivatives supply is limited.

In both the U.S. and Western Europe, the trend toward heavy-duty liquid detergents could cause some shift in choices made among the fast-growing detergent alcohol products to be used. Among the anionics, competition among LASs, alcohol sulfates, and alcohol ether sulfates could slow the growth of all, relative to the major nonionic compounds produced from detergent alcohols, alcohol ethoxylates. These compounds hold an edge because they are nonionic, a surfactant form that generally is unaffected by water hardness in performing cleaning functions. Since most liquid detergents do not contain phosphate builders to handle water hardness, alcohol ethoxylates and derivatives can have cost/performance values comparable to other alcohol surfactants.

Another advantage often cited for use of alcohol ethoxylates in formulated detergents is their ability to remove oily stains from fabrics. Although it's a widely debated view, some formulators believe the ethoxylates are better than anionics for washing garments that have high contents of synthetic fibers, especially polyesters, at low temperatures. The shift in demographics and life style in the U.S. has led to fewer dirty work clothes and fewer children's clothes in the laundry and more dress and athletic clothing containing body oil stains. That has caused formulators to partially substitute nonionic alcohol ethoxylates for LASs, spurring growth in demand. However, because alcohol ethoxylates remove body oils so well, they are seldom used in hand dishwashing or personal care products. The many industrial and institutional detergent uses of the ethoxylates also are helping growth.

Few other nonionic surfactants are consumed in large quantities in household detergents, although some have large use in industrial detergents. Alkylphenol ethoxylates have wide industrial application; fatty amine oxides and fatty alkanolamides often are used in light-duty liquid detergents and in some personal care products such as foam stabilizers.

Cationic surfactants are used in laundry detergents mainly for special properties, such as providing a softening or an antistatic effect. Small quantities are used to obtain a synergistic effect with anionics. Cationics are used in many formulations for industrial and institutional cleansers, specialty emulsifiers, and germicides. Chemically, almost all are many types of amino compounds.

Regardless of type, surfactant performance depends on the quality of the water used, a fact known since cleaners were first invented. The process of lowering the surface tension of water and improving wettability of fabrics or surfaces falls to surfactants, but this process is hindered by water hardness—the concentration of calcium and magnesium ions in water. The ions may react with surfactants and other components of a cleaner to form products that precipitate and, in effect, leave the washed item less clean than expected. To handle water hardness, builders long have been added to detergent formulations. Currently, most builders used in detergents complex or chelate the unwanted calcium and magnesium, prevent redeposition of soil, help disperse and suspend dirt, and generally improve the efficiency of surfactants.

The largest quantity of material used in detergent formulations as builders, by far, is sodium tripolyphosphate (STPP). Other builders sometimes used include such inorganic compounds as soda ash, sodium silicates, other phosphate compounds, and various zeolites. Citric acid, sodium citrate, aminopolycarboxylic acids and salts, and certain acrylic polymers account for most of the rest of the builders used in household cleaners and in institutional and industrial cleaners consumed in the U.S. In Western Europe and in other regions, some so-

Washing conditions influence detergent formulations

	Washing machines		
	U.S./Canada	Japan	Western Europe
	Agitator type	Impeller type	Drum type
Heating coils	No	No	Yes
Fabric load, kilograms	2–3	1–1.5	3–4
Wash liquor, liters	35–80	30–45	18–25
Total water consumption, regular heavy cycle, liters	140	150	120
Wash liquor ratio	1:15–1:30	1:20–1:30	1:5–1:25
Wash time, minutes	10–15	5–15	60–70 (90 °C) 20–30 (30 °C)
Wash, rinse, and spin time, minutes	20–35	15–35	100–120 (90 °C) 40–50 (30 °C)
Wash temperature, °C			
Hot	50	10–40	90
Warm	27–43	—	60
Cold	10–27	—	30–40
Water hardness (median), ppm $CaCO_3$	100	50	250
Automatic detergent addition	Mostly no	Mostly no	Dispenser
Recommended detergent dose			
Grams per liter[a]	1.5	1.3	8–10
Grams per kilogram of fabric	35–50	30–40	60–80
Peroxide bleach	b	b, c	b
Chlorine bleach	b	b, c	b, c
Drying process by automatic dryer	b	b, c	b, c

a In U.S./Canada and Japan without bleaching components. b May be commonly used. c Item considered less important. Source: Henkel

dium nitrilotriacetate is used as a builder and competes with STPP.

Despite bans on use and limitations on concentrations of phosphates in detergent formulations in various areas of the U.S. and other parts of the world, and despite growth in use of liquid laundry detergents without STPP, phosphate builders still dominate this category of components in formulated detergents and cleaners. Other builders are evaluated against STPP to determine their efficiency in detergent formulations.

Demand for STPP will decline 2 to 3% this year, according to Michael W. Berezo, Monsanto's business manager for builders and polyphosphates. The bans on phosphates in household detergents in various parts of the U.S. to reduce eutrophication (algae growth) in lakes and streams and the shift toward heavy-duty liquid laundry detergents that either don't contain builders or contain nonphosphate builders are causing the decline. Additional state bans are expected to further reduce demand for phosphate builders in powder laundry detergents.

Longer term, U.S. demand for phosphates in laundry detergents will remain unchanged at best over the next three years, says Lewis G. Furman, FMC's marketing manager for phosphorus chemicals. More likely, a decline of 5% or more may occur from 1988 levels unless bans on phosphate use are reversed.

Both Berezo and Furman agree that large markets remain for phosphate materials in detergent formulations of many kinds for the many uses other than heavy-duty laundry detergents. Monsanto, for example, has developed a special grade of material of medium density for use in making automatic dishwasher detergents, a market that is growing because of the increasing number of homes with automatic dishwashers, points out Berezo. FMC is working on phosphate systems for application to formulated liquid products for the various institutional and industrial cleaner markets, particularly commercial laundering, automatic dishwashing, and food service areas.

In the institutional and industrial market area, Monsanto offers tetrapotassium pyrophosphate (TKPP) as a highly soluble builder for use in commercial dishwashing detergents. The company notes that its sales of the compound increased 19% in 10 months of 1988. TKPP costs more than STPP, but is less soluble. To offset the cost factor, Monsanto also offers sodium trimetaphosphate, to which potassium hydroxide can be added by a formulator to get the sequestering qualities of STPP and the solubility of TKPP, Berezo says.

Other builders that are the only practical alternatives to phosphates also are used and various efforts are made to overcome their deficiencies. However, some of these builders also provide other desirable properties to formulated detergents so their use can further offset their deficiencies as builders. For example, soda ash will remove calcium ions from water by precipitation as the carbonate. But the calcium carbonate is difficult to keep in suspension and often redeposits on fabrics, giving a harsh feel and a grey tint to white clothes. It also dulls colors. But soda ash costs less than STPP. It also provides bulk in powder formulations and contributes to flow during detergent manufacture and packaging.

Sodium silicate provides alkalinity to the wash water, reduces corrosion in washing machines, aids in manufacturing (especially in spray drying), has a low cost, and provides bulk, but it does not react significantly with calcium ions in

Three derivatives consume 81% of detergent alcohol

Total 1987 consumption = 680 million lb

Source: Shell Chemical

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the water. It does contribute to deflocculation of soils and aids antiredeposition of soils and calcium precipitates. Therefore, sodium silicate and sodium carbonate often will be used together in powdered detergent formulations.

Zeolites (sodium aluminosilicates) as ion exchangers long have been found useful in detergent formulations in varying degrees. They have low solubility, so use is expected to decline for no other reason than the continued shift toward liquid detergents. Zeolites cost less than STPP, but are effective mainly on calcium ions. Often zeolites are used as a partial replacement of STPP for cost savings or as a substitute for STPP where phosphates are banned. However, they require another sequestering agent for magnesium ions. Zeolites also are included in formulations because of their ability to handle other ions, such as iron and copper, salts of which could redeposit on clothes and give undesirable results.

Use of citric acid and its salts (largely sodium) as a builder in detergent formulations is growing because of the shift toward liquids in which phosphates seldom are used. In powdered detergents, citrates are not used because of their low efficiency when compared with STPP and caking tendencies that cause problems in manufacturing. Bans on phosphates and the convenience of liquid detergents likely will push up demand for citrates in the detergent market. However, this market for citrates still will be small compared with food and beverage uses.

Most of the other chelating or sequestering products are in the large category of specialty cleaners. Their use in laundry detergents varies. But in most formulations, the concentrations are quite low, if they are used at all. Use in institutional and industrial cleaners probably accounts for the largest share of consumption.

Numerous other materials may be added to formulated detergents. These are added to perform such diverse actions as bleaching, foam regulation, solubilization, fabric softening and brightening, removal of proteinaceous stains, and prevention of redeposition of dirt. Not all of the possible materials will be in any one formulation, but most heavy-duty laundry detergents will have those needed to meet the perceived multifunctionality requirements of convenience in home use.

Bleaches also have been used to various degrees for a long time. Until the demand for convenience accelerated in the 1980s, chlorine bleaches (usually a solution of sodium hypochlorite) were added separately from the detergent. Those kinds of bleaches work well in cooler water. They can't be used in liquid-formulated products because they react with other components during standing. As a result of the deficiences in chlorine bleach, sodium perborate is the material of choice in multifunctional detergents. Sodium percarbonates and various organic peroxygens have been proposed as possible bleaching materials, but so far their commercial use is small.

Perborate bleaches are much less effective at low temperatures because of poor hydrolyzation. Higher concentrations of perborate can offset the low efficiency, but that also increases costs. To overcome that problem, a variety of bleach activators have been developed, designed to react preferentially with hydrogen peroxide from hydrolyzation of the perborate and form organic peroxy acids. The peroxy acids have higher oxidation potentials than hydrogen peroxide and provide reasonably effective low-temperature (typically below 60 °C) bleaching. In Western Europe, where most washing machines have heating elements and often washing temperatures are much higher than in the U.S. and Japan, the perborate bleaches work well without activators.

Addition of an activator and a perborate to make a detergent more multifunctional adds to the cost, and as yet it is uncertain whether consumers will pay a premium for this convenience and performance. The technology is present for perborates to be in powdered detergents, but the economics are in question, according to Linda J. Myrick, FMC's industry manager for peroxygen chemicals. As for liquids, a way to put a peroxide into a liquid detergent hasn't been found yet. FMC is actively pursuing a multifunctional molecule that will put peroxide into a bottle, Myrick adds.

A nonaqueous slurry containing liquid surfactants and a perborate might become commercial, speculates Rudi Moerch, vice president of new products and peroxygens for Degussa Corp. Moerch points out that perborates are stable in many organic systems. He also foresees dishwasher detergent formulations as slurries, but the peroxygen com-

pounds probably will be peracids and not persalts.

Besides the basic components in a detergent formulation of surfactants, builders, and bleaches, many auxiliary materials are used to impart a special property to aid the total cleaning process. Enzymes, for example, have been in and out of detergents, particularly in Western Europe, for 25 years. In the U.S., the accelerating shift toward liquid heavy-duty and nonphosphate laundry detergents over the past decade has spurred use of enzymes in the protease and amylase families. Newer developments, such as alkaline cellulases for cotton fabric treatment and a genetically engineered lipase from Novo Laboratories in Danbury, Conn., stem from efforts to supply enzymes to meet demands in making multifunctional detergents. To make more new enzymes for such detergents, Novo expects genetic engineering technology to find wide use in this area, says Robert J. Petrowski, manager for market development. In a few years, Petrowski says Novo aims to produce all of its products through use of genetically engineered microorganisms, such as customized enzymes with better catalytic efficiency and formulation compatibility.

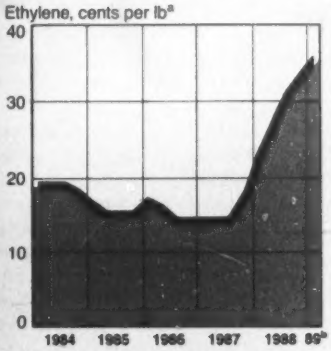
Even when well washed and bleached, most white clothing will retain a slightly yellowish color. To overcome this aesthetic problem, blue dyes began to be added to the rinse in laundering more than 100 years ago. Some of the dyes are still used, but most formulated detergents now contain optical brighteners or fluorescent whitening agents.

Chemically, these agents are complex derivatives of several classe of compounds. The most important are the stilbenes. The compound to be used in formulated laundry detergents depends on the kind of fiber to be cleaned and on washing conditions. The market for fluorescent whitening agents is growing as they become more widely used, and their concentrations in detergents, although small, increase, according to Joseph Huypen of Mobay Corp. Through its own development and purchase of other companies' product lines, Mobay offers fluorescent whitening agents that cover such requirements as light fastness, stability to chlorine, effectiveness with synthetic and wool fibers, and suitability for multifunctional detergents. Although no specific data are available, Huypen estimates U.S. demand for these agents last year at about 10 million lb.

In most laundry detergent formulations, surfactants and builders act sufficiently to remove soil from fibers and leave it in the wash liquor. Sometimes, however, the soil will be redeposited on clothes, giving a characteristic grey color that becomes deeper with repeated washings. To minimize possible soil redeposition, most formulators add materials that hinder approach of soil to fibers. For a long time, carboxymethylcellulose derivatives were used with success on cotton clothing. With the advent of synthetic fibers, various nonionic cellulose ethers have become widely used. As new antiredeposition agents with improved cost/performance properties are offered, consumption is forecast to increase.

Multifunctional detergents may include other auxiliary components to act as antistatic agents, solubilizers, and fragrances. Making multifunctional products with a dozen components to meet consumers' demands for performance, low cost, and convenience will continue to challenge detergent formulators. They will need whatever help that can come from the suppliers of detergent materials. □

Rising prices hurt ethylene-based surfactants



a Typical price on U.S. Gulf Coast. b Estimated.
Sources: Pace Co., C&EN estimates

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